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TIME DEPENDENT SOLIDIFICATION OF BINARY MIXTURES

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TIME DEPENDENT SOLIDIFICATION OF BINARY MIXTURES*

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Abstract

The problem of change of phase in a binary mixture is considered under arbitrary cooling or heating on the surface. Significantly different behavior is noted between the known solution for a sudden jump in surface temperature and other cooling histories. The solution is presented in series form, and a numerical example is given.

Introduction

The problem of solidification (or melting) of mixtures has received attention for a number of years both from fundamental and practical points of view (cf.[1]). Analytical solutions of the corresponding coupled heat and mass transfer boundary-value problem have been discussed for semi-infinite bodies under sudden changes of surface temperature (e.g.[2,3,4]). The response to these special conditions has been found to be characterized by similarity, and by constancy of concentration in the solid, and of both phases at the interface. This behavior cannot be expected to prevail in any more complex problem, whether the additional complexity be due to different cooling histories, different geometrical configurations or other effects. The purpose of the present work is to examine the problem of a semi-infinite slab, solidifying under arbitrarily time-dependent cooling conditions at the surface, and to derive a solution valid for short times after the start of solidification. In particular, it is noted that the special behavior alluded to earlier is not exhibited in the present solution.

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Formulation of the Problem

Consider a slab ($0 < x < L$), initially ($t=0$) liquid with temperature T_{Lo} and with solute concentration C_{Lo} , under prescribed cooling conditions at $x=0$ and (to fix ideas) insulated and with no mass transfer at $x=L$. Solidification will start at $x=0$ at a time t_m , i.e., when the temperature reaches the value

$$T_m(t_m) = T_o - mC_{Lo} \quad (1)$$

where $[2] T = T_o - mC_L$ is the equation of the liquidus curve in the (linearized) phase diagram of the binary mixture in question. The pre-solidification solution is easily obtained by standard methods [5], since it does not involve any coupling between heat and mass flow, and in fact corresponds to

$$C_L(x, t) = C_{Lo} \quad t \leq t_m \quad (2)$$

For $t > t_m$, the solid phase will occupy the space $0 < x < s(t)$, and the problem is then described by the following equations (for properties constant but not necessarily equal in the solid and the liquid):

Field equations:

$$K_L T_L'' - \rho c_L \dot{T}_L = 0 \quad ; \quad DC_L'' - \dot{C}_L = 0 \quad \text{in } s(t) < x < L \quad (3)$$

$$K_S T_S'' - \rho c_S \dot{T}_S = 0 \quad ; \quad DC_S'' - \dot{C}_S = 0 \quad \text{in } 0 < x < s(t) \quad (4)$$

Boundary conditions (for example):

$$-K_S T_S'(0, t) = Q_o(t) \quad \text{or} \quad T_S(0, t) = T_{So}(t); \quad C_S'(0, t) = 0 \quad (5)$$

$$-K_L T_L'(L, t) = Q_L(t) \quad \text{or} \quad T_L(L, t) = T_{LL}(t); \quad C_L'(L, t) = 0 \quad (6)$$

Interface conditions:

$$T_L(s, t) = T_S(s, t) = T_m(t) \equiv T_o - mC_L(s, t); \quad C_S(s, t) = kC_L(s, t) \quad (7)$$

$$K_S T_S' - K_L T_L' = \rho L \dot{s} \quad ; \quad D_S C_S' - D_L C_L' = (1-k) \dot{C}_L \quad \text{at } x = s(t) \quad (8)$$

To these, initial ($t=t_m$) conditions must be added, stipulating that temperature and concentration are continuous at $t=t_m$ and that

$$s(t_m) = 0 \quad (9)$$

In the above equation k is the partition coefficient, and the other symbols have obvious meanings (cf. [2])

Basic Considerations

It is convenient, in order to construct a solution to eqs. (3) to (9), to begin with some general considerations based on experience with the analogous uncoupled heat conduction problem. This eliminates the necessity of employing a direct method of solution (e.g., the embedding technique[6]) which, although applicable to the coupled problem, is likely to be rather cumbersome. What

will then be used will be an inverse method, that is one in which the form of the solution is assumed at the outset, and it is then shown that all conditions of the problem can be satisfied on the basis. To complete the solution it is then necessary to show that the solution thus found is the only possible one. The appropriate uniqueness theorem will be presented in a subsequent publication and is not considered here.

We first note that, in the uncoupled problem, a distinction must be made [7] depending on whether

$$\lim_{y \rightarrow 0} \xi(y)/\sqrt{y} = 0 \quad \text{or} \quad \lim_{y \rightarrow 0} \xi(y)/\sqrt{y} \neq 0 \quad (10)$$

where

$$\xi(y) = \frac{s(t)}{2\sqrt{\kappa_s t_m}}; \quad y = (t/t_m) - 1 \quad (10a)$$

The second of (10) is satisfied by the similarity solution earlier mentioned, which is a direct extension of the classical Neumann solution [5] of Stefan's problem. We note that, in both uncoupled and coupled solutions of this type, the form of ξ is the same, i.e., $\xi = 2\lambda\sqrt{y}$ for $y \ll 1$, where λ is a constant. We will return to that problem later; our present aim is the discussion of problems characterized by the first of (10), and we shall assume that there too the form of $\xi(y)$ is unchanged by coupling.

The form of the function $\xi(y)$ is known in a number of cases. The starting solution (i.e., the first term of series expansion) is known for any arbitrary cooling history [7]. For the general class of problem in which the surface heat flux is expressible in a series of a half-integral powers of y , it is found [7] that $\xi(y)$ is also so expressible, while for the companion problem in which the surface temperature is so expressible, $\xi(y)$ requires [8] a series in powers of $y^{1/2}$. Let us consider the former of these classes of problems, and assume that the heat flux is continuous; then [7] gives

$$\xi(y) = \sum_{n=0}^{\infty} \xi_n y^{(n+3)/2} \quad (11)$$

Inspection of the second of eq.(8) can now be used to guess the first term of a series representation for the concentration. The right-hand side of that equation is proportional to \dot{s} , or, with (11), initially proportional to \sqrt{y} . Hence it is reasonable to expect that the concentration be distributed, for short times, in the manner corresponding to a surface flux also proportional to \sqrt{y} , or

$$\frac{C_L(X,y)}{C_{Lo}} = 1 + C_{L2} y i^2 \operatorname{erfc}(XB_L \delta / \sqrt{y}) \text{ for } y \ll 1 \quad (12)$$

where

$$X = \frac{x}{2\sqrt{\kappa_S t_m}}; B_{L,S} = \sqrt{\kappa_{L,S}/D_{L,S}}; \delta = \sqrt{\kappa_S/\kappa_L} \quad (13)$$

For C_S we write a similar expression, but imaged about $X = 0$ so as to satisfy (5), or, still for $y \ll 1$,

$$\frac{C_S(X,y)}{C_{Lo}} = C_{So} + \frac{kC_{S2}}{2} y [i^2 \operatorname{erfc}(XB_S/\sqrt{y}) + i^2 \operatorname{erfc}(-XB_S/\sqrt{y})] \quad (14)$$

where the last of (7) requires that $C_{So} = kC_{Lo}$, and where the factor $k/2$ has been introduced for future convenience.

To extend the solution, it is again conjectured that a series in half-integral powers of y is appropriate, or

$$\frac{C_L(X,y)}{C_{Lo}} = 1 + \sum_{n=2}^{\infty} C_{Ln} y^{n/2} i^n \operatorname{erfc}(XB_L \delta / \sqrt{y}) \quad (15a)$$

$$\frac{C_S(X,y)}{C_{Lo}} = k \left\{ 1 + \frac{1}{2} \sum_{n=2}^{\infty} C_{Sn} y^{n/2} [i^n \operatorname{erfc}(XB_S/\sqrt{y}) + i^n \operatorname{erfc}(-XB_S/\sqrt{y})] \right\} \quad (15b)$$

Similar arguments may now be applied to the first of eqs. (8) to obtain the form of the temperature functions. In this case, one must be careful however to add particular solutions of (3) and (4) which will insure satisfaction of the non-homogeneous boundary conditions (5). The simplest way of achieving this is to employ [6,9] the analytic continuation $T^*(X,y)$, into the post-solidification period, of the pre-solidification solution. Thus

$$V_L(X,y) \equiv \frac{T_L(X,y)}{T_{Lo} - T_m(t_m)} = \frac{T^*(X,y)}{T_{Lo} - T_m(t_m)} + \sum_{n=2}^{\infty} T_{Ln} y^{n/2} i^n \operatorname{erfc}(X\delta/\sqrt{y}) \quad (16a)$$

$$V_S(X,y) \equiv \frac{T_S(X,y)}{T_{Lo} - T_m(t_m)} = \frac{T^*(X,y)}{T_{Lo} - T_m(t_m)} + \frac{1}{2} \sum_{n=2}^{\infty} T_{Sn} y^{n/2} [i^n \operatorname{erfc}(X/\sqrt{y}) + i^n \operatorname{erfc}(-X/\sqrt{y})] \quad (16b)$$

Eqs. (15) and (16) satisfy all conditions of the problem, with the exception of the conditions to be satisfied at the solid-liquid interface, namely (7) and (8). In dimensionless form, these take the following form (the arguments ξ, y being understood throughout):

$$v_L = v_S = v_o \left(1 - A \frac{C_L}{C_{Lo}} \right) \quad (17a,b)$$

$$\left(C_S / C_{Lo} \right) = k \left(C_L / C_{Lo} \right) \quad (17c)$$

$$\frac{\partial v_S}{\partial x} - \eta \frac{\partial v_L}{\partial x} = \frac{2\sqrt{\pi}}{M} \frac{d\xi}{dy} \quad (17d)$$

$$\frac{\partial (C_S / C_{Lo})}{\partial x} - \left(\frac{\delta B_S}{B_L} \right)^2 \frac{\partial (C_L / C_{Lo})}{\partial x} = 4B_S^2 (1-k) \frac{d\xi}{dy} \quad (17e)$$

where the dimensionless notation:

$$M = \frac{\sqrt{\pi}}{2} \frac{c [T_{Lo} - T_m(t_m)]}{l} ; A = \frac{mC_{Lo}}{T_o} ; v_o = \frac{T_o}{T_{Lo} - T_m(t)} ; \quad (18)$$

$$\eta = \frac{\kappa_L}{\kappa_S} ; \left(\frac{\delta B_S}{B_L} \right)^2 = \frac{D_L}{D_S}$$

The five sets of coefficients $\xi_n, C_{Ln}, C_{Sn}, T_{Ln}, T_{Sn}$ must be adjusted so as to satisfy the five equations (17a-e).

Solution and Discussion

The solution now requires the substitution of (11), (15) and (16) into (17a-e); separation of the resulting equations into terms of like powers of y , then gives sets of equations from which the unknown coefficients can be derived. The process is straight forward but rather laborious, since it requires expansion in powers of y of the several integrated error functions, whose arguments themselves are power series. The details of the process will be omitted, but it may be noted that the calculations fall in a distinct pattern. It is convenient to consider first the highest-order terms in eqs. (17a,d,e); these yield three simultaneous equations for (ξ_o, C_{L2}, T_{L2}) , and the coefficients (T_{S2}, C_{S2}) are then found from (17b,c) respectively. The pattern repeats for further coefficients: a set of three simultaneous equations for (ξ_1, C_{L3}, T_{L3}) results from the next-order terms in (17a,d,e), with (T_{S3}, C_{S3}) obtained again from (17b,c), and so forth.

As an example, the case of a constant flux Q_o at $x=0$ was considered in detail.

Here

$$\frac{T^*(X,y)}{T_{Lo} - T_m(t_m)} = \frac{T_{Lo}}{T_o - T_m(t_m)} - \sqrt{\pi(1+y)} \operatorname{ierfc} \frac{X}{\sqrt{1+y}} \quad (19)$$

and the following results are obtained (for simplicity we take $\delta = \eta = 1$ and $B_L = B_S$):

First-order terms:

$$\xi_0 = \frac{1}{\frac{3\pi}{2M} + 3\sqrt{\pi} B(1-k)AV_0} \quad (20a)$$

$$C_{L2} = C_{S2} = 6\sqrt{\pi} B(1-k)\xi_0; \quad T_{L2} = T_{S2} = 3\pi\xi_0/M$$

Second-order terms:

$$\xi_1 = \frac{-3\pi\xi_0}{\frac{8\sqrt{\pi}}{M} + 16(1-k)BAV_0} \quad (20b)$$

$$C_{L3} = C_{S3} = 32(1-k)B\xi_1; \quad T_{L3} = T_{S3} = 16\sqrt{\pi}\xi_1/M$$

Third-order terms:

$$\xi = \frac{48\sqrt{\pi}\xi_0^2 + 2M(3\sqrt{\pi}\xi_0 - 1) + 3\pi^{3/2}\xi_0\left(\frac{2M^2}{\sqrt{\pi} + 2(1-k)BAV_0M} - 3\xi_0\right) + 3B^2AV_0M(1-k)\xi_0^2[32 - 15\pi(1-k)]}{15\pi + 30\sqrt{\pi}AV_0BM(1-k)}$$

$$C_{L4} = 30\sqrt{\pi}(1-k)B^2\xi_2 + 3\sqrt{\pi}B(1-k)\xi_0^2; \quad C_{S4} = C_{L4} - 192B^2\xi_0^2(1-k); \quad (20c)$$

$$T_{L4} = \frac{6\pi}{M}\left[5\xi_2 + \left(3\sqrt{\pi}\xi_0 - \frac{2M}{\sqrt{\pi}}\xi_0\right)\right]; \quad T_{S4} = T_{L4} - 96\sqrt{\pi}\xi_0^2/M$$

and so forth. Some comments on the above solution may be useful.

The method employed for the solution makes it clear why a distinction must be made depending on which of eqs.(10) holds. In fact, when (as at present) the first of (10) is valid, the various error-function integrals tend, as $y \rightarrow 0$ and on $X = \xi(y)$, to constants independent of the problem parameters. When the second of (10) holds, in contrast, the error functions are dependent on the proportionality constant λ between ξ and \sqrt{y} . This implies, for example, that $C_L(\xi, y) \rightarrow f(\lambda)$ as $y \rightarrow 0$, and therefore $T_m(t)$ is also dependent on λ . The quantity λ would appear in all equations, and the present separation of the several equations would no longer be possible. The procedure followed here could of course still be employed, but it would be much more cumbersome. It is rather more convenient to solve the problem separately in these cases, as indeed was done in [2,3,4].

The present solution reduces to the uncoupled one [9] if either $A=0$ or $k=1$; in all other cases the form of ξ is the same but the coefficients differ. The concentration of the interface, given by

$$\frac{C_L(\xi, y)}{C_{Lo}} = \frac{1}{k} \frac{C_S(\xi, y)}{C_{Lo}} = 1 + \frac{C_{L2}}{4}y + \frac{C_{L3}}{6\sqrt{\pi}}y^{3/2} + \left(\frac{C_{L4}}{32} - \frac{B\xi_0}{\sqrt{\pi}}C_{L2}\right)y^2 + \dots (21)$$

exhibits(Fig.1) a gradual increase from its initial value. Note that the concentration in the solid is not uniform.

LIST OF SYMBOLS

Symbols listed in the [brackets] are dimensionless, and are defined in the equations indicated.

[A, eq.(18)]parameter characterizing the liquidus line
[B, eq.(13)]= $\sqrt{\kappa/D}$
cspecific heat
Cmass-fraction of solute
Ddiffusion coefficient
ffunction
kpartition coefficient
Kthermal conductivity
λlatent heat of fusion
Lthickness
mslope of liquidus line
[M, eq.(18)]principal fusion parameter
Qheat flux
s, [ξ , eq.(10a)]position of solid-liquid interface
t, [y, eq. (10a)]time
T, [V, eqs(16)]temperature
x, [X, eq.(13)]distance from exposed surface
[δ , eq.(13)] $\sqrt{\kappa_S/\kappa_L}$
[η , eq.(18)]ratio of liquid to solid diffusivities
κdiffusivity
[λ]similarity coefficient in constant temperature solution
ρdensity

Fig.1. Variation of interface concentration $C_L(\xi, y) = 2C_S(\xi, y)$ and of interface position $\xi(y)$ with time.
 $M = 0.1$; $k = A = 0.5$; $\eta = \delta = B_S = B_L = V_0 = 1$

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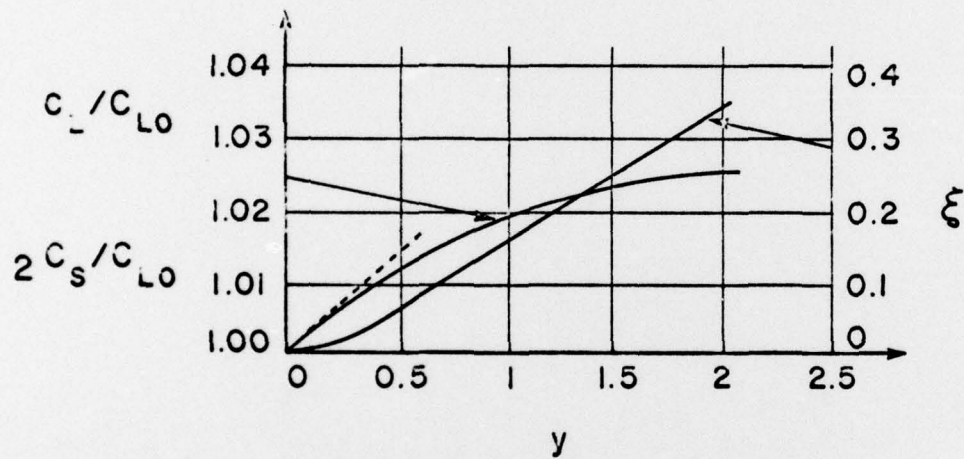


Fig. 1. Variation of interface concentration $C_L(\xi, y) = 2C_S(\xi, y)$ and of interface position $\xi(y)$ with time.
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